High-T_c superconductivity induced by doping rare earth elements into CaFeAsF

Peng Cheng, Bing Shen, Gang Mu, Xiyu Zhu, Fei Han, Bin Zeng and Hai-Hu Wen*

National Laboratory for Superconductivity, Institute of Physics and Beijing National Laboratory for Condensed Matter Physics, Chinese Academy of Sciences, P. O. Box 603, Beijing 100190, China
(Dated: December 5, 2008)

We have successfully synthesized the fluoride-arsenide compounds $Ca_{1-x}RE_xFeAsF$ (RE=Nd, Pr; x=0, 0.6). The x-ray powder diffraction confirmed that the main phases of our samples are $Ca_{1-x}RE_xFeAsF$ with the ZrCuSiAs structure. By measuring resistivity, superconductivity was observed at 57.4 K in Nd-doped and 52.8 K in Pr-doped samples with x=0.6. Bulk superconductivity was also proved by the DC magnetization measurements in both samples. Hall effect measurements revealed hole-like charge carriers in the parent compound CaFeAsF with a clear resistivity anomaly below 118 K, while the Hall coefficient R_H in the normal state is negative for the superconducting samples $Ca_{0.4}Nd_{0.6}FeAsF$ and $Ca_{0.4}Pr_{0.6}FeAsF$. This indicates that the rare earth element doping introduces electrons into CaFeAsF which induces the high temperature superconductivity.

PACS numbers: 74.70.Dd, 74.25.Fy, 75.30.Fv, 74.10.+v

Since the discovery of superconductivity in the quaternary compound $LaFeAsO_{1-x}F_x$ with $T_c = 26$ K,[1] the quest for new high-T_c superconductors in this FeAs-based family has never ceased. Especially when replacing La with other rare earth elements, a group of superconductors with critical temperature well exceeding 50 K were fabricated,[2,3,4] which excites the whole physical society. Besides these doped REFeAsO (RE = rare earth elements) superconductors with ZrCuSiAs-type structure (abbreviated as the FeAs-1111 phase), iron-based superconductors with different structures were also synthesized, such as $(Ba, Sr)_{1-x}K_xFe_2As_2$ (ThCr$_2$Si$_2$-type, FeAs-122),[5,6,7] Li_xFeAs (PbFCl-type, FeAs-111),[8,9,10] FeSe (PbO-type, FeAs-11).[11] Among them the superconductors with the FeAs-1111 phase seems to have the highest superconducting transition temperature. The highest T_c reported so far is about 56 K in $Gd_{1-x}Th_xFeAsO$.[4] Very recently a new series of FeAs-based compounds were successfully synthesized, namely fluoride-arsenides AEFeAsF (AE = divalent metals: Ca, Sr, Eu) with the ZrCuSiAs structure.[12,13,14,15] This new compound is an analogue of REFeAsO, where the $(REO)^+$ layer is replaced by $(AEF)^+$ layer. For SrFeAsF, superconductivity could emerge by either doping cobalt directly into the FeAs-layer[16] or partial replacement of Sr with rare earth elements (Lanthanum[15], Samarium[17]). While for CaFeAsF, superconductivity was also realized by doping 3d transition metals (Co and Ni) into the iron sites in the FeAs-layer with the highest T_c of about 22 K in the case of Co doping.[12,18] This relative low value of T_c could be due to the damage to the FeAs planes when substituting Fe with Co. Thus it is interesting to know whether the rare earth elements doping could get superconductors with higher critical temperatures since it is the case in La-doped SrFeAsF[15] where superconductivity at about 32 K was observed. In this paper we report the discovery of high-temperature superconductivity in $Ca_{0.4}RE_{0.6}FeAsF$ with T_c(onset) = 57.4 K by doping Nd and 52.8 K by doping Pr. The transition temperature at 57.4 K marks the highest record so far in the FeAs-based
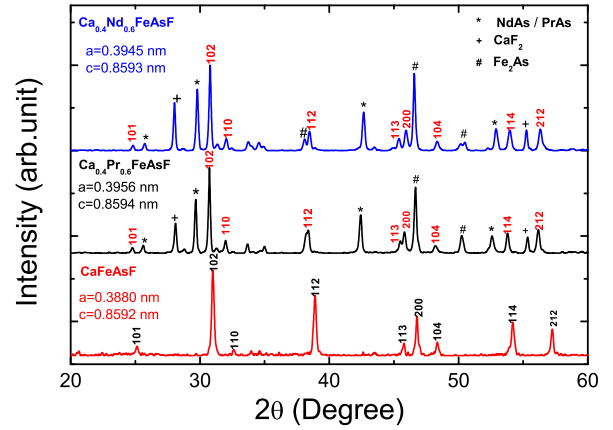

FIG. 1: (Color online) X-ray diffraction patterns for $Ca_{1-x}RE_xFeAsF$ (RE=Nd, Pr; x=0, 0.6) samples. All the main peaks can be indexed to the tetragonal ZrCuSiAs-type structure. For the doped samples, the peaks from the impurities are precisely indexed to the phases NdAs (PrAs), CaF$_2$ and Fe$_2$As.

superconductors.

The $Ca_{1-x}RE_xFeAsF$ samples were synthesized by solid-state reaction method. Firstly, CaAs, NdAs and PrAs were prepared by heating Calcium pieces (purity 99.99%), Pr pieces (purity 99.99%) and Nd pieces (purity 99.99%) with As powder (purity 99.99%) respectively at 700 ^{o}C for 10 hours. Then stoichiometric CaAs, REAs(RE = Nd or Pr), FeF$_2$ (purity 99%) and iron powder (purity 99.99%) were mixed as the nominal composition $Ca_{1-x}RE_xFeAsF$ (x=0, 0.6), grounded and pressed into a pellet. All the processes were carried out in a glove box with argon atmosphere (both H$_2$O and O$_2$ are limited below 0.1 ppm). Finally the product was sealed in a quartz tube with 0.4 bar of high purity Ar gas. It was then slowly heated up to and stayed at 900 ^{o}C for
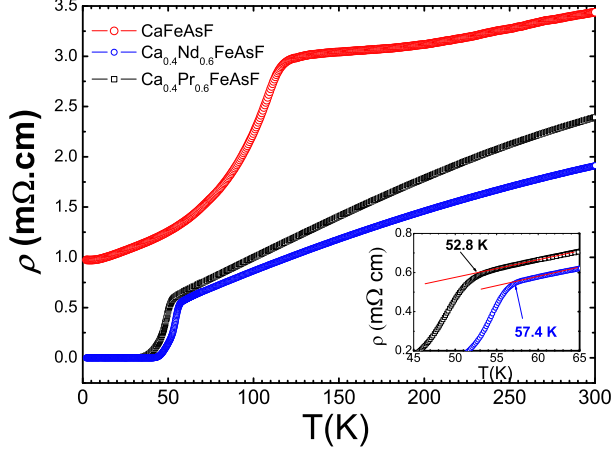
FIG. 2: (Color online) Temperature dependence of resistivity for the CaFeAsF and $Ca_{0.4}RE_{0.6}FeAsF$(RE=Nd, Pr). The inset shows an enlarged view in the region of the superconducting transition.

20 hours and followed by a treatment at 1050 ^{o}C for 20 hours.

The x-ray diffraction measurement was performed at room temperature using an MXP18A-HF-type diffractometer with Cu-K_α radiation from 10° to 60° with a step of 0.01°. The analysis of x-ray powder diffraction data was done by using the software POWDER-X[19]. The DC magnetization measurements were carried out on a Quantum Design superconducting quantum interference device (SQUID) magnetometer. The resistance and Hall-effect data were collected using a six-probe technique on a Quantum Design instrument physical property measurement system (PPMS) with magnetic fields up to 9 T.

In Fig. 1 we show the x-ray diffraction (XRD) patterns for the samples $Ca_{1-x}RE_xFeAsF$ (x=0, 0.6). One can see that the parent phase CaFeAsF is rather pure where all diffraction peaks can be indexed by the tetragonal structure with a=0.3880 nm and c=0.8592 nm. When Nd or Pr was introduced into this system some secondary phases appear, which is similar to the case in Samarium-doped SrFeAsF.[17] This is understandable since CaF_2 is a very stable compound which can be easily formed during the reaction. The left off-stoichiometric compositions will lead to the formation of $Ca_{1-x}RE_xFeAsF$, Fe_2As and NdAs or PrAs. Therefore it would be helpful for forming the superconducting phase by blocking the formation of the CaF_2 phase and thus the Fe_2As and REAs (RE=Nd and Pr). From Fig.1 one can see that all the main peaks of RE-doped samples could be well indexed to a ZrCuSiAs-type structure with a=0.3945 nm and c=0.8593 nm for $Ca_{0.4}Nd_{0.6}FeAsF$ and a=0.3956 nm and c=0.8594 nm for $Ca_{0.4}Pr_{0.6}FeAsF$, while all the other peaks were indexed precisely to the standard XRD

patterns of NdAs(PrAs), CaF_2 and Fe_2As. We all know that the radius of Pr^{3+} is around 1.01 Å and Nd^{3+} is 1.0 Å which are both a little larger than that of Ca^{2+} (0.99 Å), so the lattice parameters may expand when rare earth elements were doped into the lattice. Compared to CaFeAsF, the c-axis lattice constants of RE-doped sample does not increase obviously while the a-axis lattice constant suffers a major change (increases about 1.6% for Nd-doped samples). The similar phenomena was also observed in La-doped SrFeAsF[15] and Sm-doped SrFeAsF.[17] One may argue that the superconductivity here could be induced by the F-doped REFeAsO phase which might happen if some amount of oxygen leaked into the samples. This possibility can be however ruled out by the following arguments. Firstly, the weighing, mixing and pressing procedures were performed strictly in the glove box which limits the oxygen down to a undoubted low level. The dense pellet was sealed into a quartz tube quickly afterwards. There is no chance for much oxygen going into the sample. Secondly, we can also get a support from the detailed analysis on the x-ray diffraction data. Taking Pr-doping as an example, the typical lattice constants of F-doped PrFeAsO with $T_c = 52$ K were: a=0.3967 nm and c=0.8561 nm,[2] which could not match any main peaks in our x-ray diffraction data. It is the same case if we compare the lattice constants of the F-doped NdFeAsO and the data from our sample $Ca_{0.4}Nd_{0.6}FeAsF$. Since all the other impurity peaks could be accurately indexed to the standard XRD patterns of PrAs, CaF_2 and Fe_2As (as shown in Fig.1), no traces of F-doped (Nd or Pr)FeAsO could be detected in our samples.

Fig.2 shows the temperature dependence of resistivity for samples $Ca_{1-x}RE_xFeAsF$ (RE=Nd, Pr; x=0, 0.6). A clear resistivity anomaly was observed at about T_{an}=118 K for the parent sample which could be attributed to the structural phase transition or an anti-ferromagnetic order. For the superconducting samples this anomaly could not be seen and a superconducting transition appears at 57.4 K (onset) for Nd-doped sample and 52.8 K (onset) for the Pr-doped one. The normal state resistivity of the superconducting samples shows a metallic behavior in wide temperature region which is typical in these optimally doped FeAs-1111 superconductors.[15]

The bulk superconductivity of $Ca_{0.4}RE_{0.6}FeAsF$ samples were confirmed by DC magnetization measurement under a magnetic field of 50 Oe in zero field cooling and field cooling processes. As shown in Fig.3, the onset point of the diamagnetic transition locates at about 54 K for Nd-doped sample and 50 K for Pr-doped one. Both samples exhibit a positive background in the normal state which may come from the impurity phase Fe_2As. It is interesting to note that a small kink appears at about 14 K in the curve of M vs. T in all superconducting samples doped with Nd. But it has never been observed in the samples with Pr doping. Therefore we attribute this effect to the possible existence of the AF ordering of the Nd^{3+} ions because they have the magnetic moments.
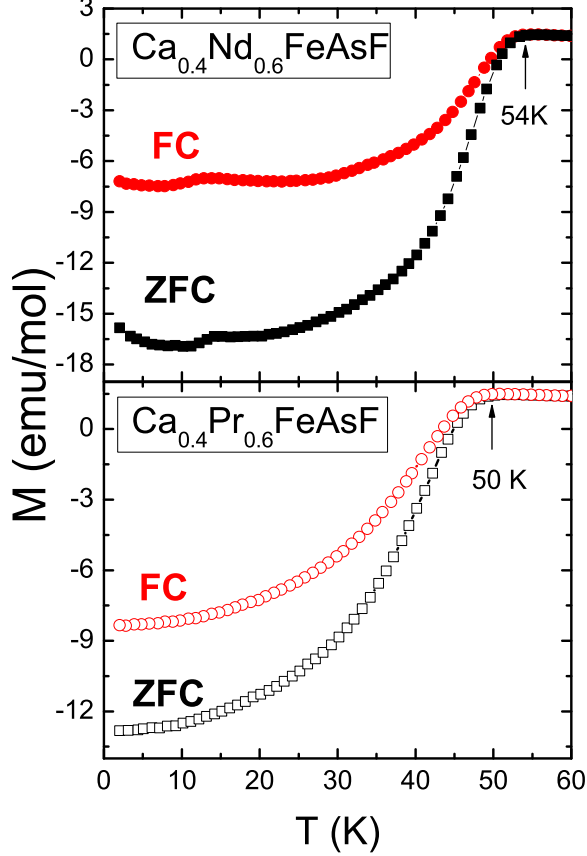
FIG. 3: (Color online) Temperature dependence of DC magnetization for samples $Ca_{0.4}Nd_{0.6}FeAsF$ and $Ca_{0.4}Pr_{0.6}FeAsF$. A DC field of 50 Oe was applied in the measurements with the zero field cooling and field cooling modes.

While for Pr^{3+} ions no magnetic moment is anticipated.

To investigate the evolution of charge carriers we conducted Hall effect measurements on our samples. For the parent compound, as shown in Fig.4, the sign of Hall coefficient changes at T_{an}=118 K. When the temperature is above T_{an}, R_H is small but negative and does not change much with temperature. While below 118 K, R_H becomes positive and increases quickly when temperature decreases. This phenomena could be attributed to the emergence of a spin-density-wave order in lower temperature region. Band structure calculations showed that the Fermi surfaces of CaFeAsF is similar to that in LaFeAsO with two electron pockets in M point and two hole pockets at Γ point[20], the SDW order removes the density of states on some Fermi pockets and may leave one of the hole pockets partially of fully ungapped thus causes the low temperature behavior of R_H[13]. Through partial substitution of Ca^{2+} with Nd^{3+} or Pr^{3+}, electrons were introduced into this system. As shown in
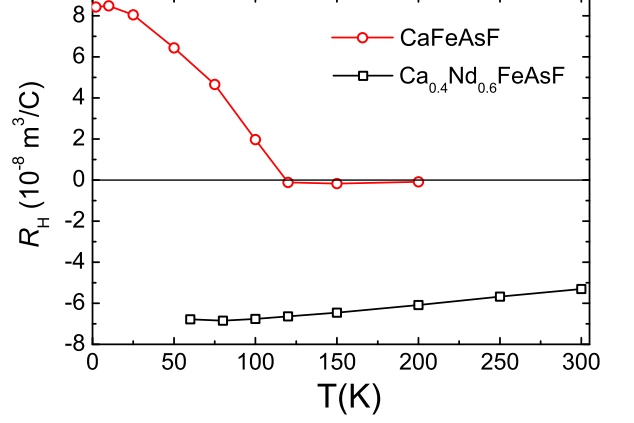

FIG. 4: (Color online) Temperature dependence of Hall coefficients R_H for samples CaFeAsF and $Ca_{0.4}Nd_{0.6}FeAsF$. The measurement was done through sweeping magnetic field at fixed temperatures.

Fig.4, the Hall coefficient R_H was found to be negative in $Ca_{0.4}RE_{0.6}FeAsF$, which confirmed that the electron-type charge carriers were doped into the system by substituting Ca partially with the tri-valent rare earth elements Nd and Pr. It should be mentioned that superconductivity was not observed in samples with low doping ($x \leq 0.2$), which may be understood that the parent phase has a hole pocket partially or fully un-gapped, thus one needs to doped more electrons into the system in order to carry out the superconductivity. If this is the case, it would be optimistic to induce superconductivity by a small amount of hole doping. This is just underway. We have so far made tens of samples which show the superconductivity beyond 50 K in the fluoride-based systems when doping about 40-60% Nd or Pr for Ca. Further efforts are worthwhile in order to get rid of the impurity phase, especially to block the formation of CaF_2 during the reaction. It remains to be found out how high the superconducting transition temperature would go if we substitute the Ca with other rare earth elements.

In summary, high-temperature superconductivity was observed in compounds $Ca_{0.4}RE_{0.6}FeAsF$ (RE=Pr, Nd). The onset superconduting transition temperature is about 57.4 K as determined from the resistivity data in $Ca_{0.4}Nd_{0.6}FeAsF$. DC magnetizations measurement confirmed the bulk superconductivity of our samples. The measurements of Hall coefficients R_H reveal the evolution of charge carriers from hole-type in the parent phase CaFeAsF to electron-type in $Ca_{0.4}Nd_{0.6}FeAsF$. Our results show that high temperature superconductivity could emerge through rare earth element doping into $(CaF)^+$ layer in this CaFeAsF system.

[*] Electronic address: hhwen@aphy.iphy.ac.cn

[1] Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, J. Am. Chem. Soc. **130**, 3296 (2008).

[2] Zhi-An Ren, Jie Yang, Wei Lu, Wei Yi, Guang-Can Che, Xiao-Li Dong, Li-Ling Sun, and Zhong-Xian Zhao, Materials Research Innovations **12**, 105-106, (2008).

[3] Z. A. Ren, W. Lu, J. Yang, W. Yi, X. L. Shen, Z. C. Li, G. C. Che, X. L. Dong, L. L. Sun, F. Zhou, and Z. X. Zhao, Chin. Phys. Lett. **25**, 2215 (2008).

[4] Cao Wang, Linjun Li, Shun Chi, Zengwei Zhu, Zhi Ren, Yuke Li, Yuetao Wang, Xiao Lin, Yongkang Luo, Shuai Jiang, Xiangfan Xu, Guanghan Cao, and Zhu'an Xu, Europhys. Lett. **83**, 67006 (2008).

[5] Marianne Rotter, Marcus Tegel, Inga Schellenberg, Wilfried Hermes, Rainer Pöttgen, and Dirk Johrendt, Phys. Rev. B **78**, 020503(R) (2008).

[6] M. Rotter, M. Tegel, and D. Johrendt, Phys. Rev. Lett. **101**, 107006 (2008).

[7] K. Sasmal, B. Lv, B. Lorenz, A. M. Guloy, F. Chen, Y. Y. Xue, and C. W. Chu, Phys. Rev. Lett. **101**, 107007 (2008).

[8] X. C. Wang, Q. Q. Liu, Y. X. Lv, W. B. Gao, L. X. Yang, R. C. Yu, F. Y. Li, and C. Q. Jin, arXiv:0806.4688(unpublished).

[9] Joshua H. Tapp, Zhongjia Tang, Bing Lv, Kalyan Sasmal, Bernd Lorenz, Paul C.W. Chu, and Arnold M. Guloy, Phys. Rev. B **78**, 060505(R) (2008).

[10] Michael J. Pitcher, Dinah R. Parker, Paul Adamson, Sebastian J. C. Herkelrath, Andrew T. Boothroyd, and Simon J. Clarke, arXiv:0807.2228(unpublished).

[11] Fong-Chi Hsu, Jiu-Yong Luo, Kuo-Wei Yeh, Ta-Kun Chen, Tzu-Wen Huang, Phillip M. Wu, Yong-Chi Lee, Yi-Lin Huang, Yan-Yi Chu, Der-Chung Yan, Maw-Kuen Wu, Proc. Natl. Acad. Sci. USA. **105**, 14262 (2008)

[12] S. Matsuishi, Y. Inoue, T. Nomura, H. Yanagi, M. Hirano, and H. Hosono, J. Am. Chem. Soc. **130**, 14428 (2008).

[13] F. Han, X. Y. Zhu, G. Mu, P. Cheng, and H. H. Wen, Phys. Rev. B **78**, 180503(R) (2008).

[14] M. Tegel, S. Johansson, V. Weiss, I. Schellenberg, W. Hermes, R. Poettgen, D. Johrendt arXiv: Condmat/0810.2120

[15] X. Y. Zhu, F. Han, P. Cheng, G. Mu, B. Shen, and H. H. Wen, arXiv: Condmat/0810.2531(unpublished).

[16] S. Matsuishi, Y. Inoue, T. Nomura, M. Hirano, and H. Hosono, J. Phys. Soc. Jpn. **77**, 113709 (2008).

[17] G. Wu, Y. L. Xie, H. Chen, M. Zhong, R. H. Liu, B. C. Shi, Q. J. Li, X. F. Wang, T. Wu, Y. J. Yan, J. J. Ying, and X. H. Chen, arXiv:0811.0761(unpublished).

[18] S. Matsuishi, Y. Inoue, T. Nomura, Y. Kamihara, M. Hirano, and H. Hosono,, arXiv:0811.1147(unpublished).

[19] C. Dong, J. Appl. Cryst. **32**, 838-838 (1999).

[20] I. A. Nekrasov, Z. V. Pchelkina, M. V. Sadovskii, arXiv:0810.3377(unpublished).